UNIT 1 - QUANTUM MECHANICS

INTRODUCTION:

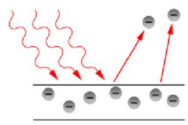
Quantum mechanics is a physical science dealing with the behaviour of matter and energy on the scale of atoms and subatomic particles or waves.

The term "quantum mechanics" was first coined by Max Born in 1924. The acceptance by the general physics community of quantum mechanics is due to its accurate prediction of the physical behaviour of systems, including systems where Newtonian mechanics fails.

DUAL NATURE OF LIGHT:

There are some phenomena such as interference, diffraction and polarization which can be explained by considering light as **wave** only.
On the other hand phenomenon such as photoelectric effect and Compton Effect can be explained by considering light as a **particle** only.
When we visualize light as a wave, we need to forget its particle aspect completely and vice versa. This type of behavior of light as a wave as well as particle is known as dual nature of light.

Einstein's theory of photoelectric effect: When a photon of energy hυ is incident on the surface of the metal, a part of energy Φ is used in liberating the electron from the metal. This energy is known as the work function of the metal. The rest of energy is given to the electron so that is acquires kinetic energy $\frac{1}{2} mv^2$. Thus a photon of energy hυ is completely absorbed by the emitter.



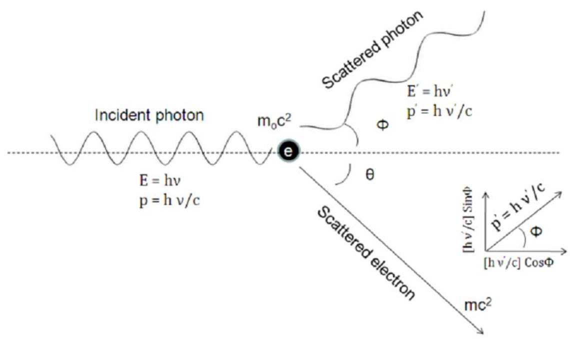
Energy of photon = Energy needed to liberate the electron + Maximum K.E of the liberated electron

$$h\upsilon = \Phi + KE_{max}$$
$$h\upsilon = \Phi + \tfrac{1}{2} mv^2_{max}$$

The above equation is called Einstein's photoelectric equation. This equation can explain all the features of the photoelectric effect.

Compton Effect

When a beam of high frequency radiation (x-ray or gamma-ray) is scattered by the loosely bound electrons present in the scatterer, there are also radiations of longer wavelength along with original wavelength in the scattered radiation. This phenomenon is known as Compton Effect.



When a photon of energy hν collides with the electron, some of the energy is given to this electron. Due to this energy, the electron gains kinetic energy and photon loses energy. Hence scattered photon will have lower energy $h\nu'$ that is longer wavelength than the incident one.

$$(\lambda' - \lambda) = h/mc\,[1-\cos\Phi] \quad \text{where } h/mc = \lambda_C = \text{Compton wavelength} = 0.02424\text{Å}$$

De Broglie hypothesis:

Louis De Broglie a French Physicist put forward his bold ideas like this

"Since nature loves symmetry, if the radiation behaves as a particle under certain circumstances and waves under other circumstances, then one can even expect that entities which ordinarily behave as particles also exhibit properties attributable to waves under appropriate circumstance and those types of waves are termed as matter waves.

All matter can exhibit wave-like behavior. For example, a beam of electrons can be diffracted just like a beam of light or a water wave. The concept that matter behaves like a wave was proposed by Louis de Broglie in 1924. It is also referred to as the de Broglie hypothesis of matter waves. On the other hand de Broglie hypothesis is the combination of wave nature and particle nature.

If ' E ' is the energy of a photon of radiation and the same energy can be written for a wave as follows

$E = mc^2$ ---(1) (particle nature) and $E = h\nu = hc/\lambda$ ---(2) (wave nature)

Comparing eqns (1) & (2) we get

$mc^2 = hc/\lambda$ or $\lambda = h/mc = h/p$

$\lambda = h/p$; where λ = De Broglie wavelength

Particles of the matter also exhibit wavelike properties and those waves are known as matter waves.

Expression for de Broglie wavelength of an accelerated electron

De Broglie wavelength for a matter wave is given by

$\lambda = h/p$; where λ = De Broglie wavelength -------------(1)

From eqn. (1) we find that, if the particles like electrons are accelerated to various velocities, we can produce waves of various wavelengths. Thus higher the electron velocity, smaller will be the de-Broglie wavelength. If velocity v is given to an electron by accelerating it through a potential difference V, then the work done on the electron is eV. This work done is converted to kinetic energy of electron. Hence, we can write

$\frac{1}{2} mv^2 = eV$

$mv = (2meV)^{1/2}$ -------------(2)

But eqn.(1) can be written as

$\lambda = h/mv$ -------------------(3)

Substituting eqn.(2) in eqn.(3) we get

$$\boxed{\lambda = h/(2meV)^{1/2}}$$

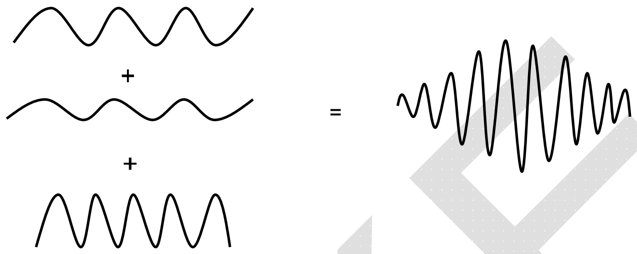
PROPERTIES OF MATTER WAVES:

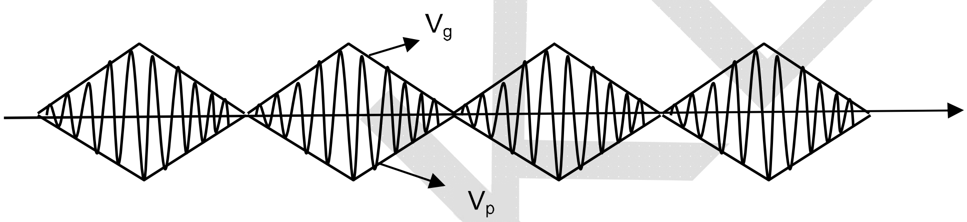
1. The wavelength of a matter wave is inversely related to its particles momentum
2. Matter wave can be reflected, refracted, diffracted and undergo interference
3. The position and momentum of the material particles cannot be determined accurately and simultaneously.
4. The amplitude of the matter waves at a particular region and time depends on the probability of finding the particle at the same region and time.

Wave packet:

Two or more waves of slightly different wavelengths alternately interfere and reinforce so that an infinite succession of groups of waves or wave packets are produced.

The velocity of the individual wave in a wave packet is called phase velocity of the wave and is represented by V_p.





Phase, Group and particle velocities:

According to de Broglie each particle of matter (like electron, proton, neutron etc) is associated with a de Broglie wave; this de Broglie wave may be regarded as a wave packet, consisting of a group of waves. A number of frequencies mixed so that the resultant wave has a beginning and an end forms the group. Each of the component waves propagates with a definite velocity called wave velocity or **phase velocity**.

Expression for Phase velocity:

A wave can be represented by

$Y = A \sin(\omega t - kx)$ ---------- (1)

Where $k = \omega/v$ = wave number (rad/m) ; ω = Angular frequency (rad/s)

When a particle moves around a circle ν times/s, sweeps out $2\pi\nu$ rad/s

In eqn.(1) the term $(\omega t - kx)$ gives the phase of the oscillating mass

$(\omega t - kx)$ = constant for a periodic wave

$d(\omega t - kx)/dt = 0$ or $\omega - k(dx/dt) = 0$ or $dx/dt = \omega/k$

$$\boxed{v_p = \omega/k}$$

When a wave packet or group consists of a number of component waves each traveling with slightly different velocity, the wave packet (group) travels with a velocity different from the velocities of component waves of the group; this velocity is called **Group velocity**.

Expression for Group velocity:

A wave group can be mathematically represented by the superposition of individual waves of different wavelengths. The interference between these individual waves results in the variation of amplitude that defines the shape of the group. If all the waves that constitute a group travel with the same velocity, the group will also travel with the same velocity.

If however the wave velocity is dependent on the wavelength the group, velocity will be different from the velocity of the individual waves.

The simplest wave group is one in which two continuous waves are superimposed. Let the two waves be represented by

$y_1 = a\cos(\omega_1 t - k_1 x)$ and $y_2 = a\cos(\omega_2 t - k_2 x)$

The resultant

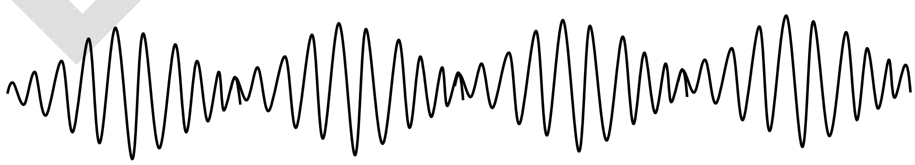
$y = y_1 + y_2 = a\cos(\omega_1 t - k_1 x) + a\cos(\omega_2 t - k_2 x)$

$$y = 2a\cos\left[\left(\frac{\omega_1 - \omega_2}{2}\right)t - \left(\frac{k_1 - k_2}{2}\right)x\right]\cos\left[\left(\frac{\omega_1 + \omega_2}{2}\right)t - \left(\frac{k_1 + k_2}{2}\right)x\right]$$

$$Let \quad \left(\frac{\omega_1 + \omega_2}{2}\right) = \omega \text{ and } \left(\frac{k_1 + k_2}{2}\right) = k$$

$$y = 2a\cos\left[\left(\frac{\omega_1 - \omega_2}{2}\right)t - \left(\frac{k_1 - k_2}{2}\right)x\right]\cos(\omega \mathrm{t} - \mathrm{kx})$$

This equation represents a wave of angular frequency ω and wave number k whose amplitude is modulated by a wave of angular frequency $(\omega_1 - \omega_2)/2$ and wave number $(k_1 - k_2)/2$ and has a maximum value of 2a. The effect of this modulation is to produce a succession of wave groups as shown below:



The velocity with which this envelope moves, i.e., the velocity of the maximum amplitude of the group is given by $v_g = \dfrac{\omega_1 - \omega_2}{k_1 - k_2} = \dfrac{\Delta\omega}{\Delta k}$

If a group contains a number of frequency components in an infinitely small frequency interval (for $\Delta k \to 0$), then the above expression may be written as

$v_g = \frac{d\omega}{dk}$ This is the expression for group velocity

Two or more waves of slightly different wavelengths alternately interfere and reinforce so that an infinite succession of groups of waves or wave packets are produced. The de Broglie wave group associated with a particle travels with a velocity equal to the **particle velocity.**

Relation between group velocity (v_g) and phase velocity(v_p)

We know that

$$v_p = \frac{\omega}{k} \quad \text{------ (1)} \qquad \text{and} \qquad v_g = \frac{d\omega}{dk} \quad \text{------ (2)}$$

$$\therefore \quad \omega = k\, v_p$$

$$\therefore \quad \mathrm{v_g} = \frac{d}{dk}(k\, v_p) = \mathrm{k}\frac{\mathrm{d}v_p}{dk} + v_p$$

$$\therefore \quad \mathrm{v_g} = v_p + \mathrm{k}\frac{\mathrm{d}v_p}{dk} = v_p + \mathrm{k}\left(\frac{\mathrm{d}v_p}{d\lambda}\right)\left(\frac{\mathrm{d}\lambda}{dk}\right)$$

$$= v_p + \left(\frac{2\pi}{\lambda}\right)\left(\frac{-\lambda^2}{2\pi}\right)\left(\frac{\mathrm{d}v_p}{d\lambda}\right)$$

$$\mathrm{v_g} = v_p - \lambda\left(\frac{\mathrm{d}v_p}{d\lambda}\right)$$

Relation between the particle velocity of a matter wave and is its group velocity

$$v_g = \frac{d\omega}{dk} \text{ -------- (1)}$$

where $\omega = 2\pi\nu = 2\pi\left(\frac{E}{h}\right)$

$$\mathrm{d}\omega = \left(\frac{2\pi}{h}\right)dE \text{ --------(2)}$$

Also, we know that

$$\mathrm{k} = \frac{2\pi}{\lambda} = 2\pi\left(\frac{p}{h}\right) = \left(\frac{2\pi}{h}\right)p$$

$$\mathrm{dk} = \left(\frac{2\pi}{h}\right)dp \text{ --------- (3)}$$

$$\therefore \frac{\mathrm{d}\omega}{\mathrm{d}k} = \frac{dE}{dp} \text{ -----------------(4)}$$

From eqn.(1) and (4) one can write

$$v_g = \frac{dE}{dp}$$

Expression for kinetic energy can be written as

$$\mathrm{E} = \frac{\mathrm{p}^2}{2\mathrm{m}}$$

$$dE = \frac{p}{m}dp$$

$$\frac{dE}{dp} = \frac{p}{m} = v_{particle} \text{ --------(5)}$$

comparing eqns.(1), (4) & (5) we get

$$\mathrm{v_{group}} = \mathrm{v_{particle}}$$

Expression for de Broglie wavelength using group velocity

We know that the expression for group velocity is given by

$$v_g = \frac{d\omega}{dk} \quad \text{--------} (1)$$

where $\omega = 2\pi\nu \Rightarrow d\omega = 2\pi d\upsilon$

$$k = \frac{2\pi}{\lambda} \Rightarrow dk = 2\pi d\left(\frac{1}{\lambda}\right)$$

$$\therefore v_g = \frac{d\upsilon}{d\left(\frac{1}{\lambda}\right)}$$

Also, we know that $v_{group} = v_{particle}$

$$\therefore v_{particle} = \frac{d\upsilon}{d\left(\frac{1}{\lambda}\right)} \quad \text{------} (2)$$

We can write

Total energy = potential energy + kinetic energy

i.e $E = \frac{1}{2}mv^2 + V$ ---- (3) also one can write $E = h\upsilon$ ----- (4)

Equating eqn.(3) & (4)

$$h\upsilon = \frac{1}{2}mv^2 + V \text{--------} (5)$$

Taking derivative on both sides of eqn.(5) we get

$h\, d\upsilon = mv\, dv$ (If we treat $V = \text{constant}$ then $dV = 0$)

$$\therefore d\upsilon = \left(\frac{mv}{h}\right) dv \text{---------} (6)$$

Substituting eqn.(6) in eqn.(2) we get

$$d\left(\frac{1}{\lambda}\right) = \left(\frac{m}{h}\right) dv$$

Taking integration on both sides we get

$$\frac{1}{\lambda} = \frac{mv}{h} + \text{const.}$$

$$\therefore \lambda = \frac{h}{mv}$$

Relation between phase velocity, particle velocity and velocity of light

Since de Broglie wave is associated with a moving particle therefore, it is very much essential to know that if both the particle and wave associated with them travel with the same velocity or with different velocity.

$$v_p = \omega/k = 2\pi\upsilon/(2\pi/\lambda) = \lambda\nu = (h/mv)(mc^2/h)$$

$$\therefore \mathbf{v_p = c^2/v}$$

As the velocity of material particle is always less than the velocity of light c, it means that the propagation velocity of de Broglie wave is always greater than c. Thus it seems that both the particle & de Broglie wave associated with the particle do not travel together with the same velocity & the wave would leave the particle behind. However, these difficulties can be ruled by considering that a moving material particle is equivalent to a wave packet rather than a single wave.

Principle of complimentarity :

The experiment of Davisson & Germer demonstrated the diffraction of electron beams. The wave nature of electrons can also be demonstrated by interference with a double slit. But it is an extremely difficult task to prepare a suitable double slit that can transmit an electron beam.

But the experiment was done by Jönson in 1961. He passed a 50,000eV beam of electron through a double slit. The pattern obtained by him was very similar to the interference pattern obtained by Young with visible light.

In an experiment of the above type it is rather tempting to try to find out through which slit an electron has passed. If we design a suitable device for detecting the passage of an electron through one of the slits, the interference pattern is found to vanish.

If the electron is to behave like a classical particle, it has to pass through one of the two slits. On the other hand, if it is a wave, it can pass through both the slits!

When we try observing the passage of electron through one of the slits, we are examining its particle aspect. However, when we observe the interference pattern we are investigating the wave aspect of electron.

At a given moment and under given circumstances the electron will behave either as a particle or as a wave but not as both.

In other words, the particle and wave nature of a physical entity cannot be observed simultaneously.

Heisenberg's Uncertainty principle.

Physical quantities like position, momentum, time, energy etc. can be measured accurately in macroscopic systems (i.e. classical mechanics). However, in the case of microscopic systems, the measurement of physical quantities for particles like electrons, protons, neutrons, photons etc are not accurate. If the measurement of one is certain and that of other will be uncertain.

A wave packet that represents and symbolizes all about the particle and moves with a group velocity describes a de Broglie wave. According to Bohr's probability interpretation, the particle may be found anywhere within the wave-packet. This implies that the position of the particle is uncertain within the limits of the wave packet. As the wave packet has a velocity spread, there is an uncertainty about the momentum of the particle. Thus according to uncertainty principle states that *the position and the momentum of a particle in an atomic system cannot be determined simultaneously and accurately. If Δx is the uncertainty associated with the position of a particle and Δp_x the uncertainty associated with its momentum, then the product of these uncertainties will always be equal or greater than $h/4\pi$. That is*

$$\mathbf{\Delta x\, \Delta p_x \geq h/4\pi}$$

Different forms of uncertainty principle

$$\mathbf{\Delta E\, \Delta t \geq h/4\pi}$$

$$\mathbf{\Delta \omega\, \Delta \theta \geq h/4\pi}$$

Applications Heisenberg's Uncertainty principle (Nonexistence of electron in the nucleus)

The radius 'r' of the nucleus of any atom is of the order of 10^{-14}m so that if an electron is confined in the nucleus, the uncertainty in its position will be of the order of $2r = \Delta x$ (say) i.e diameter of the nucleus

But according to HUP

$\Delta x\, \Delta p \geq h/4\pi$ (Δp = uncertainty in momentum)

$\Delta x \sim 2x10^{-14}$m

Therefore,

$\Delta p = h/(4\pi\, \Delta x) = 6.625E\text{-}34 / (4\pi \text{ x } 2x10^{-14}) = \mathbf{2.63 \text{ x } 10^{-21}}$ **kg-m/s**

Taking $\Delta p \sim p$ we can calculate energy using the formula

$E^2 = c^2(p^2 + m_o^2c^2) = (3x10^8)^2 x\, [(2.63 \text{ x } 10^{-21})^2 + (9.1x10^{-31})^2 x\, (3x10^8)^2]$
$= 7.932x10^{-13}J = 4957745 \text{ eV} \sim \mathbf{\mathit{5\ MeV}}$

However, the experimental investigations on beta decay reveal that the kinetic energies of electrons must be equal to 4MeV. Since there is a disagreement between theoretical and experimental energy values we can conclude that electrons cannot be found inside the nucleus.

a) Wave function (ψ)**:**

Water waves ------------ height of water surfaces varies

Light waves -------------- electric & magnetic fields vary

Matter waves -------------- wave function (ψ)

Ψ is related to the probability of finding the particle. Max Born put these ideas forward for the first time.

- The wave function ψ indicates the state of the particle. However it has no direct physical significance. There is a simple reason why ψ cannot be interpreted in terms of an experiment. The probability that something be in a certain place at a given time must lie between 0 & 1 i.e. the object is definitely not there and the object is definitely there respectively.

- An intermediate probability, say 0.2, means that there is a 20% chance of finding the object. However, the amplitude of a wave can be negative as well as positive and a negative probability -0.2 is meaningless. Hence ψ by itself cannot be an observable quantity.

- Because of this the square of the absolute value of the wave function ψ is considered and is known as probability density denoted by $| \psi |^2$

- The probability of experimentally finding the body described by the wave function ψ at the point x, y, z at the time t is proportional to the value of $| \psi |^2$.

- Small value of $|\psi|^2$ ----- Less possibility of presence
- As long as $|\psi|^2$ is not actually zero somewhere however, there is a definite chance, however small, of detecting it there. Max Born first made this interpretation in 1926.
- If we know the momentum of a particle, we can find the wavelength of the associated matter wave by using the equation $\lambda = h/mv$. We have now to realize how we can describe the amplitude of a matter wave. That is we have to find out just what is waving.

A particle of mass 'm' traveling in the increasing x- direction with no force acting on it is called a free particle.

According to Schrodinger the wave function $\psi(x,t)$ for a free particle moving in the positive x direction is given by

$\psi(x,t) = \psi_o e^{i(kx - \omega t)}$, here ψ_o = amplitude and $\psi(x,t)$ = complex

b) Probability density :

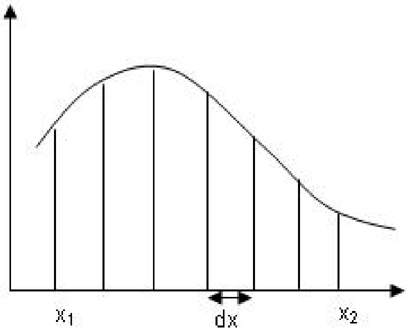
If ψ is a complex no. then its complex conjugate is obtained by replacing i by –i, ψ alone don't have any meaning but only $\psi\psi^*$ gives the probability of finding the particle. In quantum mechanics we cannot assert where exactly a particle is. We cannot say where it is likely to be

$$P(x) = \psi\psi^* = [\psi_o e^{i(kx - \omega t)}] [\psi_o e^{-i(kx - \omega t)}] = |\psi_o|^2$$

- Large value of $|\psi|^2$ ----- Strong possibility of presence of particle
- Small value of $|\psi|^2$ ----- Less possibility of presence of particle

c) **Normalization of wave function:**

The probability of finding the particle between any two coordinates x_1 & x_2 is determined by summing the probabilities in each interval dx. Therefore there exists a particle between x_1 & x_2 in any interval dx. This situation can be mathematically represented by



$$\int_{x_1}^{x_2} |\psi(x)|^2 dx = 1$$

If a particle exists anywhere in a region of space within a small volume element dv, then the normalized condition can be represented as

$$\int_{-\infty}^{+\infty} |\psi|^2 dV = 1$$

Time independent one dimensional Schrodinger wave equation :

A wave eqn. for a debroglie wave is given by

$\psi = A\,e^{i(kx-\omega t)}$ ------------- (1)

Differentiating twice eqn.(1) with respect to t we get

$$\frac{\partial^2\psi}{\partial t^2} = -\omega^2\left[A\,e^{i(kx-\omega t)}\right]$$

$\frac{\partial^2\psi}{\partial t^2} = -\psi\omega^2$ -------------- (2)

Displacement 'y' of a wave is given by $y = A\sin[\omega t - kx]$ *-------(A)*

Differentiating twice w.r.t 't' we get $\frac{\partial^2 y}{\partial t^2} = -\omega^2 y$ *----------(B)*

Similarly differentiating twice w.r.t 'x' we get $\frac{\partial^2 y}{\partial x^2} = -k^2 y = -\left(\frac{\omega}{v}\right)^2 y = -\left(\frac{1}{v}\right)^2 \omega^2 y$ *----(C)*

Comparing eqns (B) & (C) we get $\frac{\partial^2 y}{\partial x^2} = \left(\frac{1}{v^2}\right)\frac{\partial^2 y}{\partial t^2}$ ------ (3)

By analogy eqn. for a traveling de Broglie wave is given by

$\frac{\partial^2\psi}{\partial x^2} = \left(\frac{1}{v^2}\right)\frac{\partial^2\psi}{\partial t^2}$ ------ (4)

Comparing eqns. (2) & (4) $\frac{\partial^2\psi}{\partial x^2} = -\left(\frac{\omega}{v}\right)^2\psi$; where $\omega = 2\pi\nu$ and $v = \nu\lambda$

$\frac{\partial^2\psi}{\partial x^2} = -\left[\frac{4\pi^2}{\lambda^2}\right]\psi$ or $\frac{1}{\lambda^2} = -\left[\frac{1}{4\pi^2\psi}\right]\frac{\partial^2\psi}{\partial x^2}$ --------(5)

For a particle of mas 'm' moving with a velocity 'v'

Kinetic energy = ½ $mv^2 = m^2v^2/2m = p^2/2m$

But $p = h/\lambda$

Therefore, KE = $[1/\lambda^2]\,[h^2/2m]$
Substituting for $1/\lambda^2$ from eqn (5) we get

$$KE = -\left[\frac{1}{4\pi^2\psi}\right]\left[\frac{h^2}{2m}\right]\frac{\partial^2\psi}{\partial x^2} = -\left[\frac{h^2}{8\pi^2 m}\right]\left[\frac{1}{\psi}\right]\frac{\partial^2\psi}{\partial x^2}$$

Total energy is given by

$$E = PE + KE = V - \left[\frac{h^2}{8\pi^2 m}\right]\left[\frac{1}{\psi}\right]\frac{\partial^2\psi}{\partial x^2}$$

$$\frac{\partial^2\psi}{\partial x^2} = (E - V)\left[\frac{-8\pi^2 m}{h^2}\right]\psi$$

$$\boldsymbol{\frac{\partial^2\psi}{\partial x^2} + \left[\frac{8\pi^2 m}{h^2}\right](E - V)\psi = 0}$$

Properties of wave function.

Ψ should

- satisfy the law of conservation of energy i.e Total energy = PE + KE
- be consistent with de Broglie hypothesis i.e $\lambda = h/p$
- be single valued (because probability is unique)
- be continuous
- be finite
- be linear so that de Broglie waves have the important superposition property

Eigen value & Eigen function:

A wave function Ψ, which satisfies all the properties is said to be *Eigen function* (Eigen = proper)

An operator $\hat{O}$ is a mathematical operator (differentiation, integration, addition, multiplication, division etc.) which may be applied on a function $\Psi(x)$, which changes the function to another function $\Phi(x)$. This can be represented as

$$\hat{O}\,\psi(x) = \phi(x)$$

If a function is Eigen function, then by result of operation with an operator $\hat{O}$, we get the same function as

$$\hat{O}\,\psi(x) = \lambda\psi(x)$$

$\Psi(x)$ = eigen function, λ = eigen value, $\hat{O}$ = operator and $\Psi(x)$ = operand

Eg. $-\frac{d^2}{dx^2}(\sin 2x) = 4(\sin 2x)$, Here $\hat{O} = -\frac{d^2}{dx^2}$; $\lambda = 4$; $\psi(x) = \sin 2x$

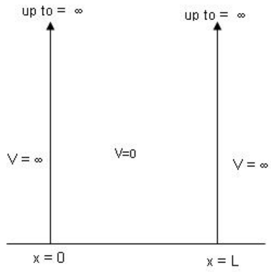
Energy Eigen values and Eigen function for a particle trapped in a potential well of infinite height

A particle moving freely in one-dimensional "box" of length 'L' trapped completely within the box is imagined to be as a particle in a potential well of infinite depth.

Initial conditions

$V(x) = 0 \; ; \; 0 < x < L$

$V(x) = \infty \; ; \; x < 0, x > L$



If the walls of the box are perfectly rigid, the particle must always be in the box and the probability for finding it elsewhere must be zero. Thus outside the box we have

$\Psi(x) = 0 \; ; \; x < 0, x > L$

Schrodinger wave equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \quad \text{--------------- (1)}$$

Inside the well V = 0, thus equation (1) becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}E\,\psi = 0 \quad \text{---------------- (2)}$$

Let $\quad \frac{8\pi^2 m}{h^2}E = k^2 \quad$ ----------------- (3)

Substituting eqn.(3) in eqn.(2) we get

$$\frac{\partial^2\psi}{\partial x^2} + k^2\,\psi = 0 \quad \text{----------------- (4)}$$

The solution for above differential eqn. can be written as

$\Psi(x) = A \sin kx + B \cos kx$ ---------------- (5)

Let us solve equation (5) outside the boundaries

<u>Case I : For $x \leq 0$, $\Psi = 0$</u>

Therefore, $\Psi(0) = A \sin 0 + B \cos 0$

=> $\mathbf{B = 0}$ ------------------- (6)

Case II : For $x \geq L$, $\Psi = 0$

Therefore, $\Psi(L) = A \sin kL$

=> $A \sin kL = 0$

=> Either $A = 0$ or $\sin kL = 0$

$A \neq 0$ because Ψ is finite inside the box

Therefore, $\sin kL = 0$

=> $k L = n \pi$

=> $\mathbf{k = n \pi / L}$ ------------------ (7)

Where $n = 1,2,3\ldots\ldots\ldots\ldots$

Thus the solution to the Schrodinger equation for a particle trapped in a linear region of length 'L' is a series of standing de Broglie waves.

Only certain values of k are permitted and thus only certain values of E may occur. Thus the energy is quantized.

Substituting eqn.(6) in eqn.(3) we get

$$\frac{8\pi^2 m}{h^2} E = \left(\frac{n\pi}{L}\right)^2 \qquad \text{or}$$

$$\boxed{E_n = \frac{n^2 h^2}{8mL^2}} \text{ ------------------- (8)} \quad \text{where } n = 1,2,3\ldots\ldots\ldots$$

Equation (8) is the expression for energy Eigen values for a particle trapped in a potential well of infinite depth.

However, the particle must be present somewhere inside the well, thus

$$\int_0^L |\psi|^2 \, dx = 1$$

Substituting eqn.(6) & eqn.(7) in eqn.(5) we get

$\Psi(x) = A \sin[n\pi / L]x$

$$\int_0^L A^2 \sin^2 \left(\frac{n\pi}{L}\right) x \, dx = 1 \qquad \text{However, we know that } \sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$$

$$\therefore \; A^2 \left[\frac{1}{2}\int_0^L dx \; - \frac{1}{2}\int_0^L \cos\left(2n\pi/L\right)x \; dx \right] = 1$$

$$\frac{A^2}{2} \left[\left[x\right]_0^L - \left\{ \left(\frac{L}{2n\pi}\right) \sin\left(\frac{2n\pi}{L}\right) x \right\} \right]_0^L = 1$$

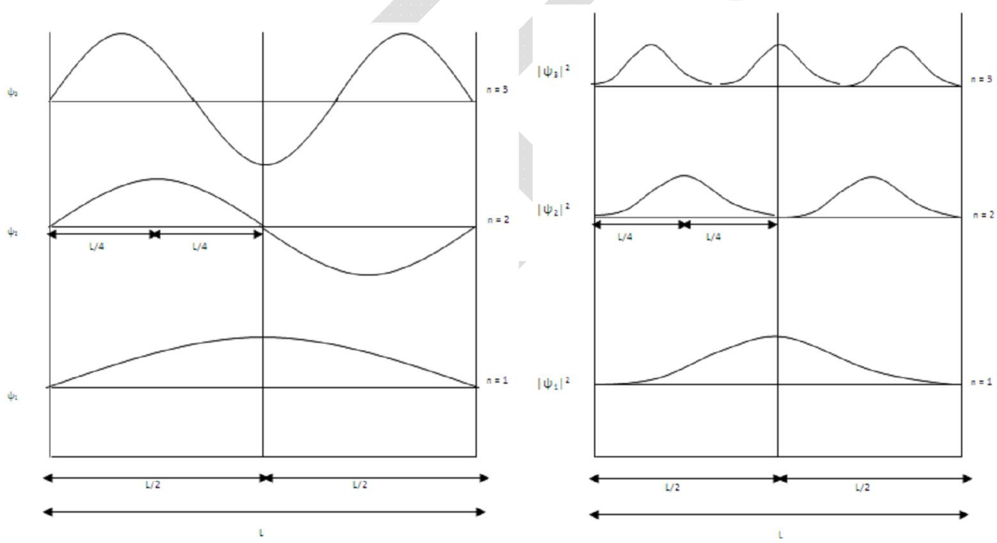
$$\frac{A^2}{2} \left[L - \left(\frac{L}{2n\pi}\right) \sin(2n\pi) L \right] = 1 \qquad \text{But} \;\; \sin 2n\pi = 0$$

Therefore,

$$\frac{A^2 L}{2} = 1 \qquad \text{or} \qquad \boxed{\mathbf{A} = \sqrt{\frac{2}{\mathbf{L}}}}$$

Hence, we can write the wave function as

$$\boxed{\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}\right) x}$$



Energy Eigen values for a free particle

A particle moving in any region of space without the influence of force is called as a free particle.

We know that Schrodinger wave equation can be written as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \quad \text{---------------- (1)}$$

Let us treat V = 0, thus equation (1) becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E \psi = 0 \quad \text{---------------- (2)}$$

Let $\frac{8\pi^2 m}{h^2} E = k^2$ ----------------- (3)

Substituting eqn.(3) in eqn.(2) we get

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0 \quad \text{----------------- (4)}$$

The solution for above differential eqn. can be written as

Ψ (x) = A sin kx + B cos kx ---------------- (5)

It is not possible to apply the boundary condition and solve the eqn. (5). Because Ψ is finite everywhere in the space. Hence energy eigen value for a free particle can be written as

$$E = \frac{h^2k^2}{8\pi^2 m} = \frac{h^2}{8\pi^2 m}\left(\frac{2\pi}{\lambda}\right)^2 = \frac{h^2}{2m\lambda^2} = \frac{\mathbf{p}^2}{\mathbf{2m}}$$

Therefore for a free particle, the energy Eigen values are not quantized and is equal to the kinetic energy of the particle itself.